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A NEW CONSTRUCTION MATERIAL-TITANIUM

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Condition and Prospects for Use of Titanium and its Alloys in the National Economy.

In the last 15 or 20 years in accordance with current plans for the development of the national economy and scientific work in the USSR a great deal of research was done in the field of metallurgy of titanium, the theory of titanium alloys; many compositions for titanium alloys were developed, and production processes for industry; work was done on the design and creation of unique industrial machinery, plants, apparatus, and testing and series operational testing was carried out. The technical and economic efficiency of using titanium and its alloys in a number of branches of industry were demonstrated.

This huge work was done by many scientific and industrial collectives of research institutes and factories of a number of ministries (non-ferrous metallurgy, aviation and ship building industries, general machine design, chemical and oil machine construction, the chemical industry and others).

Institutes of the Academy of Sciences of the USSR participate creatively in research on metallurgy, physical metallurgy, the metal chemistry of titanium, and in developing new titianium alloys, their testing and adoption in industry. The results of many studies are published by the A. A. Baykov Institute of Metallurgy of the Academy of Sciences of the USSR in collected works of conferences on titanium [1--5].

As a result of this work a great deal of titanium metallurgy has developed which is called on to provide the requirements of many branches of industry. The scientific and technical basis for the wide use of this metal are the following properties of titanium and especially its alloys: low specific weight, high strength, corrosion resistance in many agressive media, suitability for industrial production, weldability, resistance to the corrosion under stress, to concentrated stress and many others.

However, as is known, up until the present time titanium was basically used only for specialized equipment. This requirement in most branches of industry did not exceed 5--8%.

In connection with the necessity for broader utilization of attainments in the field of metallurgy of titanium and the increased efficiency of

using titanium, supplies have begun for the national economy for instruments, machines and equipment made of titanium and its alloys. The growth of the requirement for this metal in chemical machine construction in the current instructions for 1970--1975 has increased by more than four times. The main consumer (about 80%) of titanium equipment is the Ministry of the Chemical Industry.

This has caused us to take on direct participation in solving the task. It is necessary to develop correct technical policy and provision of organized technical and economic measures for the effective realization of solutions adopted.

Besides the considerable growth in production of titanium a gradual decrease in the cost of titanium sponge is envisioned. In 1975 the cost of sponge will be about 60% of its cost in 1968, and the decrease in cost of semi-manufactured goods is intended to be even greater: comparison with 1968 the cost of sheet is a total of 32--35%, that is decreased by almost 3 times.

As a result of these measures, one can plan to gradually bring the cost of titanium semi-manufactured goods close to the cost of stainless steel and nickel alloys.

If one accepts the value of chrome-nickel stainless steel in 1969 as 100%, then semi-manufactured goods made from titanium that year were approximately 6 times greater. Thanks to measures for decreasing the cost of titanium, the cost difference between stainless steel and titanium will differ in 1971 by 3.3 times, in 1975--by 2 times and in 1980--will be only about 1.3 times. An important factor in the cost of titanium semi-manufactured goods is the fact that the cost of the metal in the charge amounts to 78% of the total cost of its production. An important task in the economics of titanium production comes from this--a decrease in cost of the charge in titanium and its alloys. In connection with this one can note the following main directions for decreasing the cost of titanium production.

1. Technological directions: a) perfecting the production process of melting ingots, b) increasing the annual yield of the percent of manufactured product to ingot, c) increasing the percent of utilization of scrap for the melt, d) vacuum methods for thermal processing, e) setting up intricate shape casting of articles, f) utilization of secondary titanium, g) use of welded pipe instead of seamless, h) the use of bimetals (titanium-steel).

2. Design directions: a) decrease in weight of the articles due to the low specific weight of titanium, b) decrease in weight of the articles due to higher specific strength than steel, c) decrease in thickness of the walls of the articles taking into account the high corrosion resistance or complete immunity of titanium to a number of agressive media.

3. Operational directions: a) lengthening the service life of the articles, b) obtaining commercial products of high quality (for example, for medical preparations), c) decreasing the number of repair operations

and cutting down on expenditure time and equipment for major and current repair.

4. Alloying of titanium with elements which have considerably lower cost than titanium sponge.

Many aspects of these directions have been studied and known to metallurgy, and there is no necessity to elaborate on them in detail. However, one should turn one's attention to certain less well known and possibly controversial questions.

In production processes one should consider that it is expedient to increase the utilization of scrap for ingot melts up to 40 or 50%. This permits according to industrial data decreasing the cost of the ingot by 22 and 30%, respectively. The mastery in industrial production of vacuum annealing of semi-manufactured goods (sheet, pipe, rod and forged pieces) according to American data, permits almost completely eliminating hydrogen from the manufacturing production of titanium and its alloys, obtaining a clear surface (without etching) and increasing their quality. From the point of view of considerably decreasing the cost, attention should be given to industrial mastery and use in chemical machine building and other branches, of articles with intricate shape casting, welded pipe and especially bimetals.

In design ways for decreasing cost of production one should keep in mind that with equal strength of structural materials in the case of using titanium and its alloys one can decrease the weight of the construction by approximately 1.5--1.8 times. The utilization of high specific strength titanium alloys in comparison with the specific strength of pure titanium, aluminum alloys and alloyed steel is more efficient in this regard.

As was shown earlier [6], the specific weight (relationship of strength to specific weight of titanium expressed in km) in its relationship to the strength of these three types of materials varies so that when there is the same strength of aluminum alloys they have an advantage over titanium alloys and steel only in those cases where their strength lies in a range from 60--70 kgf/mm^2. These values for strength are the maximum attainable at the present time for strength in aluminum alloys. As will be shown below, modern titanium alloys have strength from 100--120 kgf/mm^2 and in the future will reach 150--180 kgf/mm^2. Even with the strength value of 100 kgf/mm^2 their specific strength amounts to 22.2 km. This corresponds to steel with a strength 170 kgf/mm^2. When the strength of titanium alloys is 150 kgf/mm^2 their specific strength is 33.3 km, which corresponds to the strength of steel . 260 kgf/mm^2.

Thus, even with industrially mastered titanium alloys with strength 100--110 kgf/mm^2 one can have a specific strength of approximately 1.7--1.8 times greater than that of steel materials with equal strength. Due to the high operational qualities of titanium alloys because of their corrosion resistance or complete immunity to a number of agressive media, one can decrease the weight of machines, equipment and other articles by approximately 1.5--2.0 times.

In this way, thanks to the unique combination of qualities of titanium alloys, one can attain a decreased total weight of units, machines and equipment made of titanium alloys by approximately 3--4 times and more in comparison with steel articles of equal strength. The experience of many years of manufacture and operation, for example, of titanium pumps showed actual possibilities of decreasing the weight of the pumps in comparison with those made of steel by 4--5 times [7].

It is interesting at the same time to develop a method of decreasing the cost of titanium semi-manufactured goods as a result of efficient alloying of titanium with cheaper and more available elements. Due to a number of circumstances this question up until recently did not get much attention and the composition of alloys from this point of view was almost disregarded. This direction can be called composition, that is, in the tasks of research one can begin to create those compound (compositions) of titanium alloys which in the cost of charge materials will be cheaper than sponge. These can be all the alloying elements which in pure form or in master alloy form are cheaper than titanium sponge (for example, aluminum, iron, chromium, manganese, copper, silicon and in the future, possibly, carbon, oxygen, nitrogen, and some others). The cost of these elements in pure form or in the form of master alloy, as is known, is many times cheaper than titanium sponge.

The cost of titanium alloys, economically alloyed with cheaper elements, with equal suitability for industrial production and strength will be significantly less than the cost of titanium alloys alloyed with other expensive and scarce elements, such as zirconium, niobium, molybdenum and vanadium.

Let us look at titanium and its alloys from the point of view of the possibilities of using them widely in the national economy. In the arsenal of science and technology there are compositions of titanium alloys which are suitable for production processes, are strong, cheap. They were and are used in chemical machine building. Placing great value on the problem of economic savings in compositions of titanium alloys, more than 15 years ago, there were developed alloys on the base of systems Ti--Al--Mn (a series of OT4 alloys) [5, 8] and alloys of 5-component system Ti--Al--Cr--Fe--Si (alloys of AT) [5, 9]. Today, alloys of these compositions are the most efficiently alloyed attainable and cheapest elements. One should look at and select one of these 2 series of alloys for broad industrial production and use.

Below are presented the classifications for strength and specific uses for all series and test titanium alloys which are of interest for efficient use in the national economy. They are divided into six groups of alloys with possible uses for them and are presented in Table 1.

As is apparent from Table 1, titanium alloys, efficiently alloyed, are entered in the first three groups. To these belong three brands of industrial pure titanium; five brands of alloys alloyed with aluminum and manganese; one brand of alloy alloyed only with aluminum, and three alloy brands alloyed with aluminum, chromium, iron and silicon. All these brands of titanium and its alloys provide obtaining strength in a range from 30 to 100--110 kgf/mm^2;

TABLE 1

TITANIUM AND ITS ALLOYS WITH VARYING STRENGTH, USED IN THE NATIONAL ECONOMY

a Марка сплава	b Состав (%) и предел прочности (кГ/мм²)	c Основные области применения (рабочая температура, °С)
I. Пластичные сплавы с низкой прочностью		
10 ВТ1-00 (с)	1 Технический чистый титан	2 Насосы, аппаратура, трубопроводы, теплообменники, опреснительные установки, арматура, тройники, фильтры, не требующие больших нагрузок (до 100—200°)
ВТ1-0 (с)		
ВТ1 (с)		
ОТ4-0 (с)	~1Al; ~1,0Mn	
	$\sigma_b = 30—60$	
II. Пластичные сплавы со средней прочностью		
АТ2 (с)	2,5Zr; 1,5Mo	3 Криогенная техника, теплообменники, насосы, трубопроводы, арматура, гидролизный аппарат, медицинские аппараты, приборы, опреснительные установки, колонны (до 200—300°)
ОТ4-1 (с)	2,0Al; 1,5Mn	
АТ3 (с)	3,0Al; 1,5Σ Cr, Fe, Si	
ОТ4 (с)	3,0Al; 1,5Mn	
10 ВТ5-1 (с)	5,0Al; 2,5Sn	
	$\sigma_b = 60—80$	
III. Конструкционные сплавы с повышенной прочностью		
10 ВТ4 (с)	4Al; 1,5Mn	4 Реакторы, компрессоры, сепараторы, центрифуги, экстракторы, колонны, автоклавы (до 300—450°)
ОТ4-2 (с)	6Al; 1,5Mn	
ВТ5 (с)	5 Al	
10 ВТ6 (с)	6Al; 4V	
ВТ20 (с)	6Al; 2Zr; 1Mo; 1V	
АТ4 (о)	4,5Al; 1,5Σ Cr, Fe, Si	
АТ6 (с)	6,0Al; 1,5Σ Cr, Fe, Si	
	$\sigma_b = 80—100$	
IV. Особокоррозионностойкие сплавы		
4200 (о)	Ti + 0,2Pd	5 Химическая аппаратура, устойчивая в концентрированной H_2SO_4, трубопроводы, медицинские аппараты, насосы, реакторы, сепараторы, центрифуги, приборы, автоклавы, колонны, электролизёры в расплавах хлористых солей (до 300—500°)
4201 (о)	Ti + 32Mo	
4204 (о)	Ti + 5Ta	
	$\sigma_b = 60—100$	
V. Высокопрочные, коррозионностойкие и жаропрочные сплавы		
10 ВТ3-1 (с)	5,5 Al; 2 Mo; 2 Cr; 1 Fe; 0,20 Si	7 Компрессоры, ультрацентрифуги, трубопроводы, автоклавы, сепараторы и другие изделия (до 600—700°)
ВТ8 (с)	6,5 Al; 3,5 Mo; 0,2 Si	
ВТ9 (с)	6,5Al; 3,5Mo; 2Zr; 0,2 Si	
ВТ18 (о)	6Al; 11Zr; 1Mo; 1Nb	
11 СТ1 (о)	Ti — Al — Zr — Sn	
СТ4 (о)	Ti — Al — Sn — Mo — Sr	
СТ6 (о)	Ti — Al — Zr — W	
	6 σ_b выше 100	
VI. [illegible] структурой		
ВТ14 (с)	4 Al; 3 Mo; 1 V	9 [illegible]
10 ВТ15 (о)	3 Al; 8 Mo; 11 Cr	
ВТ16 (о)	2,5 Al; 7,5 V	
ВТ22 (о)	2,5Al; 7,5Mo; 1Cr; 1 Fe 8	
	σ_b=110 — [illegible]	
	от [illegible]	

The key for this Table is on the following page (page 7).

Key for Table 1:

a. Brand of alloy
b. Composition (%) and strength (kgf/m^2)
c. Basic areas of use (operating temperature, °C)

I. Ductile alloys with low strength
1. Industrial pure titanium
2. Pumps, apparatuses, pipelines, heat exchangers, distilling equipment, fittings, T-joints, filters, not requiring large loads (from 100--200°)

II. Ductile alloys with average strength
3. Cryogenic equipment, heat exchangers, pumps, pipelines, fittings, hydrolysis units, medical equipment, instruments, distilling units, columns (up to 200--300°)

III. Structural alloys with increased strength
4. Reactors, compressors, separators, centrifuges, extractors, columns, autoclaves (up to 300--450°)

IV. Especially-corrosion-resistant alloys
5. Chemical equipment resistant to concentrated H_2SO_4, pipelines, medical equipment, pumps, reactors, separators, centrifuges, instruments, autoclaves, columns, electrolytic reduction cells in chlorine salt melts (up to 300--500° C)

V. High-strength, corrosion-resistant and heat-resistant alloys
6. Greater than
7. Compressors, ultracentrifuges, pipelines, autoclaves, separators and other articles (up to 600--700°)

VI. High-strength thermomechanically treated alloys with unstable β-structure
8. (depending on the processing procedures)
9. Compressors, ultracentrifuges, separators and other articles with thermal stability (up to 300--400°)
10. VT
11. ST

Annotation: (c)--series, (o)--test

they have for the same strength approximately the same suitability for production processes and possess ductile properties and weldability.

One can conclude from this that for the use of titanium in the national economy the most efficient and cheapest brands are those enumerated above, twelve brands of alloys which do not contain scarce and expensive alloying elements.

The question of the use in the national economy of one or another of these brands of alloys is decided by the technical requirements for strength, corrosion resistance, suitability for production processes and given technical and economic efficiency of their use. These questions are also a matter of independent judgment.

As concerns the remaining brands of titanium alloys which contain expensive and rare elements (Zr, Nb, Mo, V etc.), the question of their use in

the national economy must be looked at from the point of view of special technical requirements, for example, for materials for cryogenic equipment which operates at temperatures of liquid helium (AT2, VT5-1), at materials with high corrosion resistance to especially agressive media (ST1, 4200, 4201 and 4204), with high strength properties and heat resistance (alloys described in groups V--VI).

In this way, one can consider that for many branches of the national economy, primarily for chemical, petroleum machine construction and the chemical industry, there is a wide assortment of titanium alloys which permit orienting oneself toward the basic factors of strength, suitability for production processes, corrosion resistance and economic feasability of alloys according to their alloying elements. Questions of metallurgy and the use of titanium in these branches of industry are looked at in works [4, 5, 10, 11].

However, up unitl now, chemical machine building to a significant degree has been limited by using pure titanium which has the lowest strength of all titanium materials [10]. Differing from the American chemical industry, where about 50% of the titanium used is in the form of titanium alloys and 50% in pure form, in our domestic chemical machine building industry more than 90% of the titanium used is in the form of pure titanium (VT1. VT1-0 and VT1-00). It seems to us that the chemical designers should look at the shining example of aviation designers for effective use of high-strength titanium alloys in modern aircraft and other flying equipment. When economically utilizing alloyed titanium alloys instead of titanium one should keep in mind that preserving the specific weight of pure titanium one can cut down on weight, overall dimensions, operating area of the article and have a number of other favorable factors due to the high strength and resistance to corrosion of these alloys. In accordance with the decreased weight of the article, obviously, one can decrease their cost by approximately as much as one time, and in this way come close to the cost of the same article made from stainless steel. By completely putting this complex of technical and economic measures into practice in the chemical machine building industry in the future it would be possible to attain an even lower cost of machinery made from titanium alloys than those made from stainless steel.

In the field of research of titanium alloys there remain two completely unsolved problems--the resistance of titanium and its alloys in liquid and gaseous oxygen and temperature ranges of its resistance in atmospheres of air, oxygen, nitrogen, molecular and atomic hydrogen. In spite of a great deal of work in these directions [12--14], up until now no one has solved the problems of reliable use of titanium and titanium alloys in articles which operate in a wide temperature range in a medium of oxidizing agents and hydrogen. Further research must be done on these problems.

In recent years, along with the Institute of Chemical Machine Building, the State Institute of Applied Chemistry, the All-Union Institute of Light Alloys, the Institute of Metallurgy of the Academy of Sciences of the Georgian SSR, the All-Union Institute of Synthetic Rubber, the Artificial Fiber Factory and other chemical enterprises, we conducted systematic research on the

technological and corrosion properties of titanium alloys. The results of this work have been partially published [1--5, 15--16]; they are inadequate due to the fact that the research and testing in a number of cases was done without comparitive evaluation of the advantages and inadequacies of these or other alloys. According to the results of these tests, Table 2 shows certain information on the corrosion resistance of new titanium alloys, AT3, AT4, AT6 and ST1; Table 3 gives information on especially corrosive-resistant alloys 4201 and 4204 and some data on the strength of titanium alloy 4200. In recent years, also, a considerable amount of work has been done in testing and adopting titanium and series titanium alloys in the national economy. According to the results of much research, of corrosion testing, of some testing in operational articles made from titanium and its alloys and the prospects for their future use, one can note the following basic fields for the utilization of titanium and its alloys in the national economy.

1. In chemical and petroleum machine building and the chemical industry: VT1-00, BT1-0, VT1, OT4-1, OT4, VT4, AT3, AT4, AT6, ST1, ST6, 4200, 4201 and 4204. The question of selecting for the chemical industry efficient brands of these alloys is a matter of independent judgement.

Machines, equipment and other articles made from these titanium alloys have been developed and are in use [10, 15, 16].

2. In non-ferrous metallurgy one should note the shining example of the adoption and use of titanium by the Severonikel' Combine with great economic savings [7]. It is necessary to utilize this experience widely in other branches of industry. It is suitable here to look at the question of efficient wide use in non-ferrous metallurgy of more high-strength alloys instead of pure titanium.

3. Research at IMET [Institut metallurgii im. A. A. Baykova Institute of Metallurgy im. A.A. Baykov], of the Academy of Sciences of the USSR, IMET of the Academy of Sciences of the Georgian SSR and others have established that in the hydrolysis, food and cellulose-paper industry it is expedient besides using pure titanium to use titanium AT3 alloy for making prototype test industrial and industrial hydrolysis units for 3 m^3, for 47 m^3 and for 160 m^3, and equipment for the food industry [16].

4. For the medical industry (chemical-pharmaceutical factories, medical instruments, bacteriocidal equipment) the work of IMET of the Academy of Sciences of the Georgian SSR resulted in important proposals for the production of gallic acid and other preparations. AT-3 titanium alloy has complete immunity to medical preparations without traces of transfer of alloying elements into the solution or preparation. The decision was made to create equipment from AT3 alloy for the chemical and pharmaceutical factories.

5. One of the promising fields of use of titanium alloys is the production of compressors, in particular ammonia pipe compressors, separators, centrifuges where in the rotating units of the machines a low specific weight of material is a decisive factor in increasing the efficiency of operation.

TABLE 2 CORROSION RESISTANCE OF TITANIUM ALLOYS AT3, AT4, AT6, ST1

(a) Среда, место испытания	(b) Время испытания, час (температура, °C)	(c) Скорость коррозии, мм/год
(I) Сплав АТ3		
HCl — 20%	3000 (20°)	10,450
HNO_3 — 5%	3000	0,095
HNO_3 — 40%	1080	0,001
HNO_3 — 68%	1080	0,0007
H_3PO_4 — 30%	3000	0,0176
H_3PO_4 — 5%	240	0.0021
(1) Царская водка	3000	0,0164
H_2SO_4 — 0,6 — 0,7%, гидролизат (2)	528 (—185—190°)	0,0107—0,0043
H_2SO_4 — 10% + 0,8 вес. % (3) бихромата калия + 10 вес.% сульфата уранила	3000 (150°)	0,01
(4) $NaCl$ — 5%, хлористые соли, H_2S	250 (20°)	0,0006; 0,0048
(5) Виннокаменная кислота	1200 (75°)	0,0029
(II) Сплав АТ4		
HCl — 2%	3000	0,95
HNO_3 — 68%	1080	0,0025
H_3PO_4—5%	240 (20°)	0,0038
(6) Морская вода + 0,1% H_2O_2	6500	0,00009
(III) Сплав АТ6		
$NaCl$ — 5%	1500	0,0032
(7) Атмосфера Черного моря в районе Батуми	5000	0
(8) Морская вода в районе Батумского нефтеперегонного завода	5000	0,0015
$NaCl$ — 5%	1500 (20°)	0,0011
$NaOH$ — 5%	1500 (20°)	0,0008
$HClO_4$ — 20%	1104 (50°)	0,0007
$HClO_4$ — 75%	1104 (50°)	0,0013
(9) HNO_3 с окислами азота, 0,5% H_2S	720 (50°)	0,0012
(IV) Сплав СТ1		
NH_4Cl — 10%	240 ([illegible])	0
[illegible] — 27%		
NH_3 [illegible]	[illegible]	[illegible]

Key:
a. Medium, location of testing
b. Testing time, hours (temperature, °C)
c. Corrosion rate, mm/yr
I. AT3 alloy
1. Aqua Regia
2. Hydrolysate
3. Potassium bichromate plus 10% by weight of uranyl sulfate
4. Chlorine salts
5. Tartaric acid
II. AT4 alloy
6. Sea water
II. AT6 alloy
7. Atmosphere of the Black Sea in the region of Batum
8. Sea water in the Batum region of the petroleum refinery
9. With oxides of nitrogen
IV. ST1 alloy

TABLE 3 CORROSION RESISTANCE OF 4200, 4201, 4204 ALLOYS WITH DIFFERENT AGRESSIVE MEDIA*

a Марка сплава	b Среда	c Температура испытаний, °С	d Время испытаний, час	e Скорость коррозии мм/год
1 ВТ1	2 Этиленхлоргидрон, кислотность 5,6%	100	100	
	3 жидкая фаза			45,812
	4 паровая »			20,734
ОТ4	3 жидкая »			14,413
	4 паровая »			9,836
4201	3 жидкая »			0,1962
	4 паровая »			0,0944
4201	5 Синтез дифенилпропана	40	1400	
	3 жидкая фаза			0,001
	4 паровая »			0,0017
4201	6 Синтез смолы ВБФС-4, pH-1	96	1000	
	3 жидкая фаза			0,001
	4 паровая »			0,0001
4201	H_2SO_4 30—35 г/л, 7 Na_2SO_4 15—20 г/л, 7 $ZnSO_4$ до 7 г/л, 8 ЛПС, H_2S, CS_2 — следы 9	95—97	2400	0,000
4201	H_2SO_4 40—45 г/л, Na_2SO_4 40—50 г/л, $ZnSO_4$ 15—20 г/л, ЛПС, H_2S, CS_2 — следы 9	97—99	1440	0,0077
4200	»	97—99	1440	0,0967
4204	»	97—99	1440	0,0452
10 4201, сварной шов	»	97—99	1440	0,0074
4204	11 Дисульфонат гидроксиламин, H_2SO_4 115 г/л 7	105—118	1300	0,0067
4201	12 Очистка сернистого газа SO_2 — 12%, H_2SO_4 до 12 г/л 13	32—45	1032	0,003
4200	»	32—45	1032	0,14—0,19
4204	»	32—45	1032	1,0

Key:

a. Brand of Alloy
b. Medium
c. Test temperature, °C
d. Testing time, hours
e. Corrosion rate mm/yr
1. VT
2. Ethylene chlorlhydron, acidity 5.6%
3. Liquid phase
4. Vapor phase
5. Synthesis of diphenylpropane
6. Synthesis of VBFS-4 resin, pH--1
7. g/1
8. Less than 7 g/1
9. LSP, H_2S CS_2--traces
10. Welded seam
11. Disulfonate hydroxylamines
12. Purifying of sulfuric gas
13. Less than 12 g/1

*4201 and 4204 alloys seem to be completely resistant to a number of media in the production of rare-earth elements with significant concentrations of HCl (up to 420 g/1). Titanium and its low-alloy alloys are not resistant in these media.

6. An important field of use for titanium alloys is power engineering. The use of these alloys for making working blades of turbines, parts for compressors and other machines show great technical and economic efficiency. The accumulated experience of institutes and enterprises in this direction guarantees broad adoption of titanium in this branch of engineering.

7. The use of titanium in the construction of distillation units for distilling sea water and purifying contaminated industrial and waste water is very promising. In the USA a great deal of work is being done in this direction and the use of titanium for these purposes appears promising. For one distilling factory, the demand for titanium is 10--15 thousand tons. In connection with these tests, one should note that there is a negative role [17] in the high content of aluminum in the alloy because of the corrosion of titanium alloys in sea water at high temperatures. Appropriate proposals are adopted on the question of using titanium and its alloys in this branch.

8. The use of titanium in transtportation, for example in maritime ship building is promising. One should also discuss the important role of the consumption of titanium and its alloys in civil aviation. The use of titanium alloys in the automobile industry and railway machine building should be considered in the future.

9. One can suppose that titanium and its alloys in the future will also be used in instrument building, agricultural machine building, electrical engineering industries, and construction of highway machinery and in other fields. To this one can add the electronic industry where titanium can be used not only as a getter but also as a structural material for vacuum radio-electronic equipment.

10. One should note the possibility of using titanium alloys as a material for decorative, architectural items or structures. There is some experience in this regard in the example of the remarkable obelisk in Moscow in honor of the victory of our country in the conquest of space. One can hope that the artists and sculptors will create yet another masterpiece of art from titanium.

The use of titanium and its alloys in the main branches of the national economy is not limited to the areas mentioned. As our knowledge of titanium and its alloys increases, the cost of the alloys decreases, broad popularization of the efficiency of the use of titanium will result in new object for its use.

One can foresee broadening of the industrial production of titanium in the next 10--20 years. If one supposes [11] that when the cost of semi-manufactured goods made from titanium is 2--3.5 dollars per kilogram (in capitalist countries) the volume of its production in the next 10 years will be 200--250 thousand tons per year, and one can consider that at the beginning of the XXI century the production of titanium in the entire world will reach approximately 500 thousand tons in a year.

The task of our scientists and engineers is to provide the leading role in Soviet titanium metallurgy in world wide production and consumption of this wonderful metal.

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Section III Corrosion Properties and Use of Titanium and Its Alloys

Oxidizability of IVT1 Titanium β-Alloy and its Protection from Gas Corrosion

The work sets forth the results of research on the kinetics of oxidation of titanium beta-alloy IVT1 which contains 7% Mo; 5.5% Cr; 3% Fe; 3% Al. IVT1 alloys belong to metastable titanium β-alloys which combine high technological ductility in a quench-hardened state, necessary for the manufacture of complex articles (σ_b to 100 kfg/mm^2, δ = 16%; ψ = 60%), with high strength and satisfactory ductility after aging (σ_b = 142--170 kgf/mm^2, δ = 10--7%, ψ = 22--11%) [1]. The alloy, after cooling from the β-field in water, in air and from the furnace preserves a β-solid solution structure. Temperature of transition $\beta \rightarrow (\alpha+\beta)$--750--800°. After aging in a temperature range 450--550° for 50--15 hours, the alloy has a structure ($\alpha + \beta$), with a ratio of phase approximately 48% β-phase and 52% α-phase.

Interest has been shown in research on the effect of phase transitions on the kinetics of oxidation of an alloy in β-state, especially in the case of $\beta \rightarrow (\alpha+\beta)$-transformation which occurs at relatively low temperatures. Literature has relatively little research on oxidation of β-alloys of titanium. In work [2] the results of research on the kinetics of oxidation of VT15 alloy are described; they were done by a method of continuous oxidation for short time intervals (4 hours). Considering that the majority of titanium alloys oxidize intensively at high temperatures a considerable amount of work has been done on protecting these alloys from gas corrosion [3--7]. They show that the best protective properties for coatings on titanium are obtained from multi-component melts [6]. In this regard, new data on protection from oxidation of titanium β-alloys are of interest.

Experiment method. Research on the kinetic effects of oxidation was done on samples 11 X 11X 4 mm, as the most satisfactory kinetic and electron-diffraction studies in both states: in β-state after quench hardening in water from 800°, 1 hour and in $\alpha + \beta$-state after quench hardening and aging at 550°, 15 hours with subsequent air cooling. Preparation of the samples for kinetic research was done by the method described in work [8]. The kinetics of oxidation were studied by a gravimetric method when heating samples in a temperature range 300--1000° in the ambient atmosphere in an ordinary muffle furnace for 50 hours. Weighing of the samples was done on analytic scales with a sensitivity $2 \cdot 10^{-5}$ g. The samples were annealed and weighed along with the crucibles. The furnace temperature was measured by a platinum-platinum-rhodium thermocouple and held with a precision of ± 5°.

Each point on the kinetic curve was obtained from five identically prepared samples. With the purpose of protecting the alloy samples from oxidation at high temperatures a layer of aluminum was applied to them with a gas-plasma jet with a thickness of the layer ~ 0.3 mm, and then coating of the sample was subjected to thermal-diffusion annealing in a vacuum (residual pressure ~ 10^{-4} mm mercury column) at 800°, 1 hour. The phase composition of the coating and scale in the samples was determined by a method of electron-diffraction and X-ray diffraction analyses.

<u>Results of experiments and discussion of them</u>. Research done showed that the sensitivity of scales used in the work was inadequate for quantitative characteristics of the oxidation process of IVT1 alloy in the range 300--500°. In this interval, the oxide films on the samples of IVT1 alloy had the form of temper colors. From this it follows that low-temperature decomposition of metastable β -phase titanium to $\alpha + \beta$ -state does not result in a change in the rate of oxidation of the alloy. Probably this fact can be explained because transformation occurs at low temperatures during which the diffusion activity of the atoms is low.

The results of kinetic research on the IVT1 alloy at 600--1000° are presented in Figure 1. An analysis of these experimental data shows that oxidation of IVT1 alloy in a range of 600--800° can be described as the function

$$(\Delta P/S)^n = kt, \qquad (1)$$

where ($\Delta P/S$) is the increase in weight per unit of area, mg/cm^2; t--time, hr; k = constant; the value of n is close to 2, that is, the process of oxidation of the IVT1 alloy occurs according to principle, close to parabolic.

Oxidation of the alloy samples at 900° during the first 4--5 hours occurs according to a principle determined by equation (1), n $\approx$ 1.4; and then--according to the linear principle with the value of the rate constant k = 0.73 mg/cm^2 · hr. At 1000°, oxidation of the alloy occurred according to the linear principle with somewhat decreased velocity constant--from 2.75 at the beginning to 2.50 mg/cm^2 · hr at the conclusion of oxidation. Spectral analysis done on the content of molybdenum in the original samples of the alloy and after oxidation for 24 hours showed that the content of molybdenum in the latter was somewhat less than in the initial samples. The decrease in rate constant in the process of oxidation can be explained by the evaporation of the oxide MoO_3.

Experimental data on research of oxidizability of the alloy shows that depending on time, the principle of oxidation in turn is transformed from gradated to linear. As a temperature increases, the time interval of transformation and the principle of oxidation is shortened. For the rate constants k_π of parabolic principle of oxidation in Figure 2, a graph is presented of the relationship of ln k_π to inverse temperatures. From the graph it is apparent that the relationship of the change of the rate constants to temperature can be presented as a binomial equation in the form

$$k_\text{п} = A_1 e^{-\frac{Q_1}{RT}} + A_2 e^{-\frac{Q_2}{RT}}, \qquad (2)$$

where Q_1 and Q_2 are the energy of activation of low and high-temperature oxidation, and A_1 and A_2 are respectively the constant values which are determined from the graph equal to: Q_1 = 52.20 kcal/mole; A_1 = 1.61 · 10^9 mg/cm^2 · hr; Q_2 = 81.40 kcal/mol; A_2 = 4.49 · 10^{14} mg/cm^2 · hr.

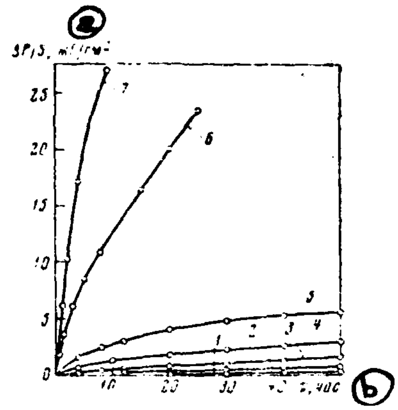

Figure 1. Kinetic Curves of Oxidation of IVT1 Alloy.

T, °C: 1--600; 2--650; 3--700; 4--750; 5--800; 6--900; 7--1000

Key:
a. Mg/cm²
b. Hr

From the data presented in Figure 2 it is apparent that at about 750° a change in the value of the energy of activation occurs which can be explained as a phase transformation in the alloy from $\alpha + \beta \rightarrow \beta$. Thus, kinetic studies support the conclusion of authors [1] concerning the idea that high-temperature phase transformation in the IVT1 alloy occurs in an interval of 750--800°.

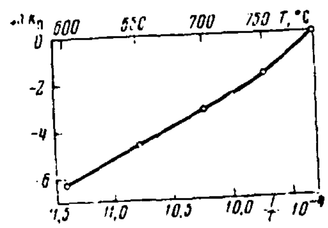

Figure 2. Graph of Temperature Relationship of Rate Constants of the Parabolic Principle of Oxidation

For comparative evaluation of oxidation-resistant properties of titanium alloys, Figure 3 shows curves of the relationship of average values of the rate of oxidation for titanium iodide, IVT1 alloy and alloys on a base of α-titanium, ST4 and ST5. An analysis of these curves shows that in the temperature range being studied, the average rate of oxidation of the IVT1

alloy is 2--3 times less than the average rate of oxidation of titanium iodide, but larger than the average rate of oxidation of the ST5 alloy; however, with an increase in temperature this difference levels out. An analysis of Figures 2 and 3 supports the opinion given earlier [3, 7] on the effect of allotropic transformation $\alpha \longrightarrow \beta$ for titanium and its alloys on a base of α-titanium and for oxidation of IVT1 alloy on a base of β -titanium.

The results of research on phase composition of scale in the samples of the alloy are presented in the Table.

RESULTS OF RESEARCH ON PHASE COMPOSITION OF SCALE

a T, °C	b Фазовый состав окалины на образцах			
	c без покрытия		f покрытых алюминием	
	d по электронограммам	e по рентгенограммам	d по электронограммам	e по рентгенограммам
300—500	TiO_2	—	—	—
600—800	TiO_2	TiO_2	γ-Al_2O_3	γ-Al_2O_3
900	TiO_2	$TiO + TiO_2$	γ-Al_2O_3	γ-Al_2O_3
1000	.	$TiO + TiO_2$	γ-Al_2O_3	γ-Al_2O_3

Key:
- a. T, °C
- b. Phase composition of scale in samples
- c. Without coating
- d. According to electron-diffraction pattern
- e. According to X-ray diffraction pattern
- f. Coated with aluminum

Typical electron diffraction patterns from the surface layer of the scale are presented in Figure 4 where there is sharply apparent the texture which can result at 500° and stays up to 800°. Studies of a cross section of creep scale by a metallographic method in crossed-over polarizers show that it is multi-layer in cross section; however, X-ray diffraction research shows only the presence of TiO_2 (rutile). Isolated phases of oxides of alloyed elements were not observed by us. A TiO phase was observed in samples of IVT1 alloy which was oxidized at 900 and 1000°, on the boundary between the alloy and the layer of scale which consists of TiO_2. Thus, peeling of the scale occurred in our case along the boundary TiO--TiO_2.

According to the data of X-ray analysis, coatings which form on samples of IVT1 alloy consist mainly of $TiAl_3$ which can possibly contain in the form of a solution other alloy elements of the alloy. The average rates of oxidation of the IVT1 alloy with a coating are presented in Figure 3. From a comparison of curves 1 and 5 it is apparent that the coating causes a significant decrease in the rate of oxidation of samples of this alloy. Thus, for example, at 1000° it is 12 times less than the rate of oxidation of samples without coating. The results of research on the phase composition

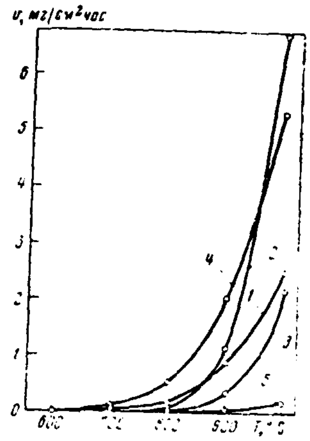

Figure 3. Curves of the Relationship of Average Rates of Oxidation to Temperature.

1--IVT1 alloy; 2--ST4 alloy; 3--ST5 alloy; 4--Titanium iodide; 5--IVT1 alloy coated with aluminum, annealing at 800°; 1 hour

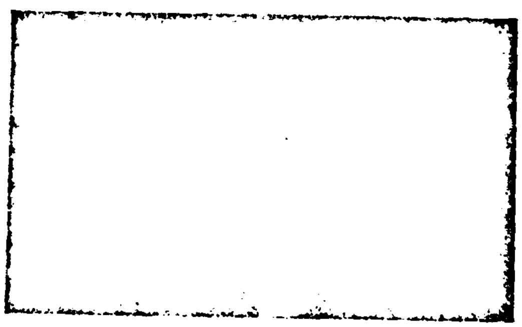

Figure 4. An Electron Diffraction Pattern From Scale on IVT1 Alloy at 500°.

of scale in samples are shown in the Table. Proceeding from the date obtained one can assert that the protective properties of the coating are explained by the formation on the surface of an oxide film which consists of γ-Al_2O_3, and which adheres well to the base. From a comparison of data obtained on average rate of oxidation of the IVT1 alloy, coated with aluminum and industrial titanium coated with aluminum [5] it follows that the aluminized alloys of titanium are more efficient than titanium.

Conclusions

1. Low-temperature tranformation $\beta \rightarrow (\alpha + \beta)$, which occurs in the alloy does not affect the kinetic oxidation of the IVT1 alloy.

2. The change in rate constants of the parabolic principle of oxidation at 740° can be explained by phase transformation $(\alpha + \beta) \rightarrow \beta$.

3. Surface alloying with aluminum effectively decreases the rate of oxidation of the alloy at high temperatures; for example, at 1000° the rate of oxidation of samples coated with aluminum decreases by 12 times.

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Compatability of Titanium Alloys with Solutions of Hydrogen Peroxide

As is known structural materials used for the production of Perhydrol must have not only high corrosion resistance but also must not have a catalytic effect on the decomposition of hydrogen peroxide. Of metallic materials, aluminum in which the admixture of iron and copper does not exceed respectively, 0.3 and 0.05% best meets this requirement [1]. However, the low mechanical properties of aluminum do not permit its use for shaping equipment for the process of obtaining hydrogen peroxide by oxidation of secondary alcohols. This process is done at 120^{o}, pressure 10 kgf/cm^2 in thick-walled reactors, completely made from Kh18N10T. Because of the high requirements for purity of process solutions, the stainless steel is also used in all manufacturing stages of the process; therefore its expenditure for equipment in large-tonnage production is very great. Replacing the steel with titanium alloys in these production processes is very promising.

There are no literary data on the compatability of titanium alloys with hydrogen peroxide. It is known that compounds of titanium very easily form with hydrogen peroxide complex compounds which catalyze the decomposition of H_2O_2 [2--4]. Therefore, even in cases with an insignificant rate of corrosion of titanium alloys, ions of titanium going into solution will cause decomposition of hydrogen peroxide. There is also the possibility of heterogeneous decomposition of H_2O_2 on the surface of Ti. All of this can result not only in a decrease in output of hydrogen peroxide but even in a more serious consequence which involves catalytic decomposition of hydrogen peroxide in an organic medium. Extremely high requirements for corrosion resistance of titanium alloys in media which contain hydrogen peroxide result from this. Then ordinary methods of corrosion research in particular the method of weighing, are inadequately sensitive for these demands.

This work is the first attempt to clarify the compatability of titanium alloys with aqueous solutions of hydrogen peroxide; its results permit one to plan directions for further research for the practical use of some of these materials under production conditions and the use of Perhydrol. Samples of industrial titanium brand VT1 and titanium alloys of known brands (OT4, AT3, AT4, AT6, AT8, VT5, VT14, ST1V, ST3 and ST4N) were approved by the tests, and also test alloys of Ti--Al systems made at the A. A. Baykov Institute of Metallurgy of the Academy of Sciences of the USSR. Testing was done in solutions of hydrogen peroxide with specified concentration (from 3 to 60%) at 20^{o} for 360 hours with constant ratio of solution volume to the surface of the sample, equal to 3 ml/cm^2. Pure solutions of hydrogen peroxide are made by diluting a 60% solution obtained by rectification of commercial hydrogen peroxide in glass equipment in a vacuum. After removing the samples the solution was analyzed for concentration of H_2O_2 and titanium ions [5]. With low loss of weight in the samples, the rate of corrosion was considered to be the quantity of Ti in the solution. The test results are presented in Tables 1 and 2.

Of all the materials tested the least resistant was brand VT1 titanium. The rate of its corrosion increases with the concentration of H_2O_2. Correspondingly, there increases the concentration of titanium compounds in the solution and the degree of decomposition of H_2O_2. Solutions of H_2O_2 (30 and 60%)

TABLE 1 CORROSION RESISTANCE OF TITANIUM ALLOYS
(360 hr; 20°, V/S = 3 ml/cm²)

a Материал	b v, г/м²·час	c $[H_2O_2]_{исх}$, %	d $[H_2O_2]_{кон}$, %	e [Ti], г/л	f Вид раствора
1 Без металла	—	2,9	0,6	—	Без изменения 2
	—	30,0	0,8	—	То же 3
	—	60,8	0,0	—	»
4 ВТ1, лист	0,0017	3,0	1,2	0,016	Светло-желтый 5
	0,0180	9,9	5,2	0,048	Желтый 6
	0,1146	30,0	30,0	0,440	Ярко-желтый 7
	0,1698	60,8	59,0	0,189	Ярко-желтый гель 8
9 ВТ1, пруток	0,0017	3,0	1,4	0,010	Слегка желтый 10
	0,0117	9,9	7,4	0,096	Желтый 6
	0,0583	30,0	30,0	0,116	Ярко-желтый 7
ВТ1, пруток оксидированный	0,0001	3,0	0,9	0,002	Без изменения 2
	0,0001	9,9	1,8	0,002	То же 3
	0,0003	30,0	7,7	0,008	»
	0,0028	60,8	11,0	0,026	Светло-желтый 5
ОТ4	0,0008	3,0	1,0	0,009	Слегка желтый 10
	0,0146	9,9	6,0	0,146	Желтый, мутный 11
	0,0363	30,0	22,6	0,030	Желтый, мутный, со взвешенным белым осадком 12
	0,0100	60,8	22,4	0,115	Ярко-желтый 7
АТ3	0,0009	3,0	0,9	0,002	Светло-желтый 5
	0,0015	10,0	6,5	0,019	»
	0,0042	30,0	18,5	0,046	Ярко-желтый 7
	0,0030	60,8	25,4	0,003	Желтый 6
АТ4	0,0019	3,0	0,8	0,003	Слегка желтый, мутный 13
	0,0026	10,0	5,6	0,028	Желтый 6
	0,0052	30,0	18,2	0,060	Ярко-желтый 7
	0,0028	60,8	26,8	0,004	Желтый 6
АТ6	0,0006	3,0	0,9	0,006	Слегка желтый 10
	0,0016	9,9	4,2	0,014	То же 3
	0,0034	30,0	19,0	0,034	»
	0,0083	60,8	46,0	0,100	Желтый, слегка мутный 14
АТ8	0,0002	3,0	1,2	0,002	Без изменения 2
	0,0014	9,9	4,1	0,014	То же 3
	0,0019	30,0	11,8	0,020	»
	0,0035	60,8	26,6	0,041	Светло-желтый 5
15 СТ1В	0,0006	2,9	0,7	0,008	Без изменения 2
	0,0004	10,0	4,2	0,014	То же 3
	0,0003	30,0	11,0	0,004	»
	0,0006	60,8	20,7	0,014	»
16 СТ3	0,0005	2,9	0,9	0,006	Без изменения 2
	0,0003	9,6	3,1	0,014	То же 3
	0,0007	30,0	9,5	0,021	»

Continuation of Table 1 and Key on following page (page 22).

Материал	v, г/м²·час	$[H_2O_2]$исх, %	$[H_2O_2]$кон, %	[Ti], г/л	Вид раствора
СТ4Н	0,0005	2,9	0,7	0,006	Без изменений
	0,0003	9,6	2,7	0,004	То же
	0,0006	30,0	9,4	0,008	»
ВТ5	0,0044	30,0	23,3	0,053	Светло-желтый
ВТ14	0,0095	30,0	20,6	0,009	Желтый, мутный

Key:

a. Material
b. V, g/m^2 · hr
c. Initial
d. Concentrated
e. g/l
f. Type of solution
1. Without metal
2. Unchanged
3. Ditto
4. VT1, sheet
5. Light yellow
6. Yellow
7. Bright yellow
8. Bright yellow gel
9. VT4, rod
10. Slightly yellow
11. Yellow, cloudy
12. Yellow, cloudy with white precipitant in suspension
13. Slightly, yellow, cloudy
14. Yellow, slightly cloudy
15. ST1V
16. ST3
17. ST4N
18. VT5
19. VT14
20. Yellow, cloudy

decompose completely in the testing time. Then the 60% solution was transformed into a transparent gel. Thermal oxide coating of titanium, brand VT1, in air at 750° for 12 hours sharply increases its corrosion resistance and decreases its catalytic activity. OT4 alloy was somewhat more resistant than VT1 brand titanium and therefore causes less decomposition of 30 and 60% hydrogen peroxide. As distinguished from VT1 brand titanium and most of the other alloys it is passivated in a 60% solution, therefore the rate of its corrosion has its maximum at 30% H_2O_2.

Type AT alloys possess a considerably larger corrosion resistance than VT1 brand titanium and OT4 alloy, but all of them still cause a considerable decomposition of H_2O_2. The AT3 and AT4 alloys were observed to have a certain tendency toward passivation with an increased concentration of H_2O_2 from 30 to 60%. However, with no substantial difference observed in the behavior of AT3, AT4, and AT6 alloys. In this way, the increase in content of aluminum in the alloy from 3 to 6% had almost no effect on its corrosion behavior. VT5 and VT14 alloys behaved analogously. Alloy AT8 was somewhat more resistant and catalytically less active. Type ST alloys had the greatest corrosion resistance and the least activity which apparently, is due to the high content in them of Al (ST3) or together with the Al also

TABLE 2 CORROSION RESISTANCE AND CATALYTIC ACTIVITY OF ALLOYS OF Ti--Al SYSTEMS (360 hr, 30% H_2O_2, 20°, V/S = ml/cm²)

[Al], %	v, г/м²·час	$[H_2O_2]$кон, %	[Ti], г/л	Вид раствора	Вид поверхности после испытаний
5	0,001	12,4	0,017	Без изменений	Темно-синяя с блеском и пятнами коричневого цвета
10	0,0005	11,6	0,006	То же	Темная, сине-коричневая с золотистыми пятнами
14	0,0006	9,8	0,007	»	Темная, сине-золотистая с блеском
18	0,0004	11,4	0,004	»	Коричнево-синяя с блеском
20	0,0002	8,9	0,002	»	Блестящая, сине-золотистая
24	0,0002	7,4	0,002	»	То же

Key:
a. V, g/m² · hr
b. Con.
c. g/l
d. Appearance of solution
e. Appearance of surface after testing
1. Unchanged
2. Dark blue with luster and spots of a brown color
3. Ditto
4. Dark, blue-brown with gold spots
5. Dark, blue-gold with luster
6. Brown-blue with luster
7. Brilliant, blue-gold

Sn (ST1V and ST4N). Both of these components are corrosion resistant in solutions of H_2O_2 and catalytically inert in relation to it [1]. However, even these alloys cause a considerable decomposition of hydrogen peroxide. It is possible that during lengthy static contact of the solution on the surface of these alloys, heterogeneous catalysis on the surface of the alloy prevails over homogeneous catalysis which causes the dissolved compounds of titanium. One must note that all the tested alloys except brand VT1 titanium and OT4 alloy in a 30% solution of H_2O_2 are covered with oxide films of varying shades--from gold to dark blue.

For purposes of clarifying the effect of the aluminum content in the alloy on its compatability with hydrogen peroxide, the behavior of test samples of alloys with content of aluminum from 5 to 24% in a 30% solution of H_2O_2 was studied. The results of these tests are presented in Table 2. All test alloys were more corrosion resistant and accordingly catalytically less active than type AT alloys. A tendency is noted for a decrease in catalytic activity of an alloy with an increase in the content of aluminum in the alloy. One must not consider the results obtained as satisfactory. However they do permit one to hope that on a base of a Ti--Al--Sn system one can obtain an alloy compatable with hydrogen peroxide under dynamic conditions, that is, when there is brief contact of the liquid with the surface of the metal which is what occurs under production conditions of hydrogen peroxide.

Conclusions

1. Alloying titanium with aluminum and tin sharply increases its

corrosion resistance and decreases its catalytic activity in solutions of H_2O_2.

2. It was established that the most corrosion resistant and least active alloy was type ST.

3. Thermal oxide coating of VT1 brand titanium in air increases its corrosion resistance by 10 times.

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